

PATENT ABSTRACTS OF JAPAN

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(54) THERMOPLASTIC ELASTOMER COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new thermoplastic elastomer composition which has flexibility and has excellent formability, rubbery characteristics, mechanical strength, compression permanent set, and a vibration-damping property.

SOLUTION: This thermoplastic elastomer composition comprises (A) an isobutylene block copolymer comprising a polymer block consisting mainly of isobutylene and a polymer block consisting mainly of an aromatic vinyl compound and (B) a modified isobutylene block copolymer which comprises the block copolymer comprising isobutylene and an aromatic vinyl compound and having alkenyl groups at the terminals.

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CLAIMS

[Claim(a)]

[Claim 1] The thermoplastic-elastomer constituent which comes to blend the denaturation isobutylene system block copolymer (B) which are an isobutylene system block copolymer (A) containing the polymer block which makes a subject the polymer block and aromatic series vinyl system compound which make an isobutylene a subject, and a block copolymer containing the polymer block which makes a subject the polymer block and aromatic series vinyl system compound which make an isobutylene a subject, and has an alkenyl radical at the end [claim 2] A denaturation isobutylene system block copolymer (B) is a thermoplastic-elastomer constituent according to claim 1 with which an allyl group is introduced into an end by the substitution reaction of an allyl compound trimethyl silane and chlorine.

[Claim 3] The thermoplastic-elastomer constituent according to claim 1 or 2 with which a thermoplastic-elastomer constituent constructs a bridge dynamically in a denaturation isobutylene system block copolymer (B) at the time of melting kneading of an isobutylene system block copolymer (A) and a denaturation isobutylene system block copolymer (B).

[Claim 4] The thermoplastic-elastomer constituent according to claim 1 or 2 characterized by a denaturation isobutylene system block copolymer (B) constructing a bridge beforehand before being mixed with an isobutylene system block copolymer (A).

[Claim 5] from the polymer block (a) with which the block which constitutes an isobutylene system block copolymer (A) and/or a denaturation isobutylene system block copolymer (B) makes an isobutylene a subject, and the polymer block (b) which makes an aromatic series vinyl system compound a subject — becoming — (b)-(a)— the thermoplastic-elastomer constituent according to claim 1 to 4 which is the triblock copolymer in which the structure of (b) is shown.

[Claim 6] The thermoplastic-elastomer constituent according to claim 1 to 5 which furthermore contains a plasticizer (C).

[Claim 7] The thermoplastic-elastomer constituent according to claim 6 with which a plasticizer (C) is chosen from paraffin series and naphthene straight mineral oil and which is a kind at least.

[Claim 8] The thermoplastic-elastomer constituent according to claim 1 to 7 which furthermore contains a cross linking agent (D).

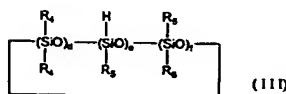
[Claim 9] The thermoplastic-elastomer constituent according to claim 8 whose cross linking agent (D) is a hydrosilyl radical content compound.

[Claim 10] A denaturation isobutylene system block copolymer (B) is a thermoplastic-elastomer constituent according to claim 1 to 5 which weight average molecular weight is 1000-500,000, and is the block copolymer which has at least 0.2 alkenyl radicals at the end per molecule.

[Claim 11] The thermoplastic-elastomer constituent according to claim 1 to 5 characterized by carrying out 10-300 weight section content of the denaturation isobutylene system block copolymer (B) with which the alkenyl radical was introduced into the end to the isobutylene system block-copolymer (A) 100 weight section.

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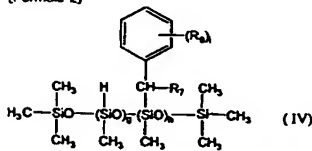
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(As for R₄ and R₅, the alkyl group of carbon numbers 1-6 or a phenyl group, and R₆ show the alkyl group or aralkyl radical of carbon numbers 1-10 among a formula) $\text{O}(\text{C}=\text{C})=\text{C}$ and e express $2(\text{C}=\text{C})$, and f expresses the integer of $\text{O}(\text{C}=\text{C})-\text{C}$, and C fills $3(\text{C}=\text{C}+\text{f})=10$, etc., — a compound can be used. What compatibility with the (B) component is especially expressed with the following general formula (IV) to from the point of being good, among the compounds which have the further above-mentioned hydrosilyl radical (Si-H radical) is desirable.

[0025]

[Formula 2]



(Among a formula, g and h are integers and are $2 \leq g+h \leq 50$, $2 \leq g$, and $0 \leq h$). R7 may express a hydrogen atom or a methyl group, and R8 may have one or more rings by the hydrocarbon group of carbon numbers 2-20, i is the integer of $0 \leq i \leq 5$.

[0026] Although the denaturation isobutylene system block copolymer (B) and cross linking agent by which the alkeryl radical was introduced into the end are mixable at a rate of arbitration, it is desirable that the mole ratio of an alkeryl radical and a hydrosilyl radical is in the range of 0.2-5 from the field of hardenability, and it is still more desirable that it is especially 0.4-2.5, if a mole ratio becomes five or more, bridge formation is inadequate, if smaller than constituent profit *** with reinforcement of enough, and 0.2, since an activity hydrosilyl radical remains in large quantities into a constituent, after bridge formation will be uniform, and a constituent with reinforcement will not be obtained.

[0027] Although the crosslinking reaction of a copolymer (B) and a cross linking agent (D) advances by mixing and heating two components, in order to advance a reaction more quickly, it can add a hydrosilylation catalyst. It is not limited especially as such a hydrosilylation catalyst, for example, radical initiators, such as organic peroxide and an azo compound, and a transition metal catalyst are mentioned.

[0028] It is not limited especially as a radical initiator. For example, G-t-butyl peroxide, 2, 5-dimethyl-2, 5-Jl-(t-butylperoxy) hexane, 2, 5-dimethyl-2, 5-Jl-(t-butylperoxy)-3-hexyne. Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha'-bis(t-butylperoxy) isopropylbenzene, Benzoyl peroxide, p-chloro benzoyl peroxide, m-chloro benzoyl peroxide, 2, 4-dichlorobenzoyl peroxide, diacyl peroxide like lauryl peroxide, Peroxy-acid ester like perbenzoic-acid-t-butyl, fault JI carbonic acid disopropyl, Peroxi dicarbonate [like fault JI carbonic acid G-2-ethylthyl] G-1, and 1-Jl-(t-butylperoxy) cyclohexane, 1, and 1-Jl-(t-butylperoxy) - Peroxy metal like 1, 3, and 5-trimethyl cyclohexane etc. can be mentioned.

[0029] Moreover, a complex with the thing which it is not limited [thing] especially as a transition metal catalyst, for example, made support, such as a platinum simple substance, an alumina, a silica, and carbon black, distribute a platinum solid-state, chloroplatinic acid, chloroplatinic acid, alcohol, an aldehyde, a ketone, etc., a platinum-olefin complex, and a platinum (0)-diaryl tetramethyl disiloxane complex are mentioned. As an example of catalysts other than a

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If loadings exceed the 300 weight sections, a problem will arise in a fall and moldability of a mechanical strength. Moreover, the demand characteristics further doubled with each application at the constituent of this invention are accepted. In the range which does not spoil physical properties, a reinforcing agent and a bulking agent, for example, a styrene-butadiene-styrene block copolymer (SBS) and a styrene-isoprene-styrene block copolymer (SIS). Moreover, elastomers, such as a styrene-ethylene butylene-styrene block copolymer (SEBS) which hydrogenated them, and a styrene-ethylene propylene-styrene block copolymer (SEPS). In addition to this, the antioxidant of a hindered phenol system or a hindered amine system, an ultraviolet ray absorbent, light stabilizer, a pigment, a surfactant, a reaction retarder, a flame retarder, a bulking agent, a reinforcing agent, etc. can be blended suitably.

[0037] As most desirable constituents of the thermoplastic elastomer, the constituent of this invention denaturation isobutylene system block-copolymer (B) 100-300 by which the alkeryl radical was introduced into the end to the isobutylene system block-copolymer (A) 100 weight section -- weight -- the section -- Preferably to a plasticizer (C) 0 -- the 100 weight sections, and a pan an isobutylene -- a system -- a block copolymer -- (--- A ---) 100 -- weight -- the section -- receiving -- an end -- the alkeryl -- a radical -- introducing -- having had -- denaturation -- an isobutylene -- a system -- a block copolymer -- (--- B ---) 50 - 150 -- weight -- the section -- a plasticizer -- (--- C ---) zero - 50 -- weight -- the section -- and -- a cross linking agent -- (--- D ---) -- having blended -- a constituent -- it is, In this case, to the denaturation isobutylene system block-copolymer (B) 100 weight section in which the alkeryl radical was introduced into the end, a cross linking agent (D) is 0.01 - 20 weight section, and a bridge formation assistant has desirable 0 - 20 weight section.

[0038] Moreover, especially the manufacture approach of the thermoplastic-elastomer constituent of this invention is not limited, but if an isobutylene system block copolymer (A), the denaturation isobutylene system block copolymer (B) with which the alkenyl radical was introduced into the end, and the above-mentioned component used by the case are the approaches which may be mixed by homogeneity, it can adopt all.

[0039] When constructing a bridge dynamically in the denaturation isobutylene system block copolymer (B) with which the alkynyl radical was introduced into the end and manufacturing the thermoplastic-elastomer constituent of this invention at the time of melting mixing of an isobutylene system block copolymer (A) and the denaturation isobutylene system block copolymer (B) with which the alkynyl radical was introduced into the end, it can carry out preferably by the approach of illustrating below.

[0040] For example, when manufacturing using direct-vent-system kneading equipment or batch type kneading equipments, such as a lab PURASUTO mill, Brebender, a Banbury mixer, a kneader, and a roll, melting kneading can be carried out until it mixes beforehand all components other than a cross linking agent and a bridge formation assistant, and a bridge formation catalyst and becomes homogeneity, and the approach of adopting how a cross linking agent and a bridge formation assistant, and a bridge formation catalyst are added subsequently to it, and crosslinking reaction fully stops melting kneading can be adopted.

[0041] Moreover, when manufacturing using the melting kneading equipment of continuous system like a single screw extruder and a twin screw extruder 11, pellets, after carrying out melting kneading of all the components other than a cross linking agent and a bridge formation assistant, and a bridge formation catalyst until it becomes homogeneity with melting kneading equipments, such as an extruder, beforehand. After carrying out the dryblend of a cross linking agent and a bridge formation assistant, and the bridge formation catalyst to the pellet, melting kneading is further carried out with melting kneading equipments, such as an extruder. How to manufacture the thermoplastic-elastomer constituent which constructs a bridge dynamically in a non-isobutylene system block copolymer (A) and consists of a bridge formation object of the isobutylene system block copolymer (A) of this invention, and the denaturation isobutylene system block copolymer (B) with which the alkeryl radical was introduced into the end. Or melting kneading of all the components other than a cross linking agent (D) and a bridge formation assistant, and a bridge formation catalyst is carried out with melting kneading equipments, such as an extruder. Add a cross linking agent and a bridge formation assistant, and

platinum compound, RhCl (PPh₃)₃, RhCl₃, RuCl₃, Ir-Cl₃, FeCl₃, AlCl₃, PdCl₂ and H₂O, NiCl₂, and TiCl₄ grade are mentioned. These catalysts can be used independently, and it does not matter even if it uses two or more kinds together. Although there is especially no limit as an amount of catalysts, it is good for using in the range of 10–1 to ten to 8 mol to use in the range of 10–3 to ten to 6 mol often and preferably to one mol of alkeryl radicals of the (B) component. If fewer than ten to 8 mol, hardening will not fully advance. Moreover, since the hydrosilylation catalyst is not desirable to use in ten to 8 mol or more, platinum catalysts containing vinyltrimethylsilane is [among these] the most desirable in respect of compatibility, bridge formation effectiveness, and scorching stability.

[0030] Moreover, for radical crosslinking, it is desirable to make a catalyst share. As a catalyst, radical initiators, such as organic peroxide, are used as a catalyst. It is not limited especially as a radical initiator. For example, G-t-butyl peroxide, 2, the 5-dimethyl-2, 5-Jl (t-butylperoxy) hexane, 2, the 5-dimethyl-2, 5-Jl (t-butylperoxy)-3-hexyne, Dialkyl peroxide like dicumyl peroxide, t-butyl cumyl peroxide, alpha, and alpha-bis(t-butylperoxy) isopropylbenzene, Benzoyl peroxide, p-chloro benzoyl peroxide, m-chloro benzoyl peroxide, 2, 4-dichlorobenzoyl peroxide, diacyl peroxide like lauroyl peroxide, Peroxy-acid ester like perbenzoic-acid-t-butyl, fault, Jl carboxic acid diisopropyl, Peroxi dicarbonate [like fault Jl carboxic acid G-2-ethylthyl], 1, and 1-Jl (t-butylperoxy) cyclohexane, 1, and 1-Jl (t-butylperoxy)- Peroxy ketal like 3, 3, and 5-trimethyl cyclohexane etc. can be mentioned. 2, the 5-dimethyl 2, 5-Jl (tert-butylperoxy) hexane, 2, the 5-dimethyl 2, and 5-Jl (tert-butylperoxy) hexyne-3 are [among these] desirable in respect of odor nature, coloring nature, and scorching stability.

[0031] The loadings of organic peroxide are iso BUCHIRE at the time of addition of organic peroxide. The range of 0.5 - 5 weight section is desirable to the N system block-copolymer 100 weight section.

[0032] The constituent of this invention can blend the bridge formation assistant which has an ethylene system partial saturation radical on the occasion of the bridge formation processing by organic peroxide. An ethylene system partial saturation radical is a polyfunctional methacrylate monomer like a divinylbenzene, a polyfunctional vinyl monomer like a triaryl SHIANU rate or ethylene glycol dimethacrylate, diethylene-glycol dimethacrylate, triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylolpropanetriethacrylate, and allyl compound methacrylate etc. These may be used independently or may use at least two or more sorts. With such a compound, homogeneity and efficient crosslinking reaction are expectable.

[0033] In order to be easy to deal with ethylene glycol dimethacrylate and triethylene glycol dimethacrylate, to have a peroxide solubilization operation and to work as a distributed assistant of peroxide also especially in it, since the homogeneity and bridge formation thermoplastic elastomer which was effective and was able to balance hardness and rubber elasticity is obtained, the bridge formation effectiveness by heat treatment is desirable.

[0034] Below 20 weight sections of the addition of the above-mentioned bridge formation assistant are desirable to the denaturation isobutylene system block-copolymer (B) 100 weight section. When 20 weight sections are exceeded, there is an inclination for independent gelation of a bridge formation assistant to tend to progress, and there is a problem in respect of cost.

[0035] In the constituent of this invention, since a moldability and flexibility are raised further in addition to an isobutylene system block copolymer (A) and the denaturation isobutylene system block copolymer (B) which has an alkynyl radical at the end, a plasticizer (C) can also be added further, the straight mineral oil used as a plasticizer (C) in the case of processing of rubber — or liquefied or the synthetic softener of low molecular weight can be used.

[0038] As straight mineral oil, although the high-boiling point petroleum component of paraffin series, a naphthene, and an aromatic series system is mentioned, the paraffin series and the naphthene which do not check crosslinking reaction are desirable. As liquefied or a synthetic softener of low molecular weight, although there is especially no limit, polybutene, hydrogenation polybutene, liquid polybutadiene, hydrogenation liquid polybutadiene, and the Pori alpha olefins are mentioned. These plasticizers (C) can use one or more sorts. As for the loadings of a plasticizer (C), it is desirable that it is the 10 - 300 weight section to the isobutylene system block-copolymer (B) 100 weight section in which the alkyl radical was introduced into the end.

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a bridge formation catalyst from the middle of the cylinder of an extruder there, and melting kneading is carried out further. A bridge is dynamically constructed in the denaturation isobutylene system block copolymer (B) with which the alkyl radical was introduced into the end. The approach of manufacturing the thermoplastic-elastomer constituent which consists of a bridge formation object of the isobutylene system block copolymer (A) of this invention and the denaturation isobutylene system block copolymer (B) with which the alkyl radical was introduced into the end etc. is employable.

[0042] In performing the above-mentioned method of performing dynamic bridge formation to melting kneading and coincidence, 150–210-degree-C temperature is desirable. Moreover, in this case, an isobutylene system block copolymer (A) cannot cause crosslinking reaction, but can construct a bridge in the denaturation isobutylene system block copolymer (B) with which the alkynyl radical was introduced into the end.

[0043] the denaturation isobutylene system block copolymer with which the alkenyl radical was beforehand introduced into the end — strange — the bridge formation object of (B) is manufactured, and when mixing the bridge formation object with an isobutylene system block copolymer (A) and adjusting the thermoplastic-elastomer constituent of this invention, the approach of illustrating below is adopted preferably.

[0044] To the denaturation isobutylene system block copolymer with which the alkynyl radical was introduced into the above-mentioned end, for example, a cross linking agent and a bridge formation assistant, Add a bridge formation catalyst and it fully kneads at suitable temperature using the kneading machine usually used for manufacture of a rubber bridge formation object. After adopting suitable bridge formation temperature and bridge formation time amount for the obtained kneading object using the press machine etc. and advancing crosslinking reaction, The bridge formation object of the denaturation isobutylene system block copolymer (B) with which it ground after cooling and the alkynyl radical was introduced into the end can be obtained, and the thermoplastic-elastomer constituent of this invention can be manufactured by carrying out melting mixing of the bridge formation object with an isobutylene system block copolymer (A).

[0045] any of the known apparatus currently conventionally used for manufacture of thermoplastics or a thermoplastic-elastomer constituent as melting aligation of the bridge formation object of the denaturation isobutylene system block copolymer (B) with which the alkyl radical was introduced into the end on that occasion, and an isobutylene system block copolymer (A) — although — it can adopt, for example, can carry out using a lab PURASITO mill, a Banbury mixer, a single screw extruder, a twin screw extruder, and other melting kneading equipments, and melting kneading temperature has desirable 150–210 degrees C.

[0046] The thermoplastic elastomer constituent of this invention can be fabricated using the molding approach and shaping equipment which are generally adopted to a thermoplastics constituent, for example, can carry out melting shaping by extrusion molding, injection molding, press forming, blow molding, etc. Moreover, since it excels in the moldability and the compression set property, the thermoplastic-elastomer constituent of this invention can be effectively used as sound deadeners, such as a sound deadener for seal material, such as a packing material, a sealant, a gasket, and a plug, CD damper, a structural damper, an automobile, a car, and home electronics, a vibrationisolating material, automobile interior material, a cushioning material, daily electronics, an electrical part, electronic parts, a sport member, a grip or shock absorbing material, wire covering material, a packing material, various containers, and stationary components.

[0047]
[Example] Although this invention is further explained below at a detail based on an example, this invention does not receive a limit at all by these. In addition, in advance of an example, various measuring methods, an appraisal method, and an example are explained.

[0048] (Degree of hardness) Based on JIS K 6352, the test piece used 12.0mm ** press sheet.
[0049] (**** breaking strength) Based on JIS K 6251, the test piece pierced and used 2mm thickness press sheet for the No. 3 mold by the dumbbell. The speed of testing was considered as a part for 500mm/.

[0050] (**** elongation after fracture) Based on JIS K 6251, the test piece pierced and used

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